My First Try

2005-02-13

The Cell

As a proof-of-concept run I built a small cell using a PE screw top jar, about 500 ml in volume. Two high density graphite electrodes fitted with threaded brass contacts were screwed through the lid and a 12.5 mm PVC vent tube was glued into the lid to discharge the gasses produced safely out the window. Additionally a 25 ml syringe was fitted through the lid to allow topping up during operation.

The Run

The cell was charged with about 400 ml of saturated Potassium Chloride solution and the level noted. A high current DC supply was connected to the electrodes and the voltage adjusted to deliver 3 Amps to the cell. Although the supply was capable of delivering up to 25 A it can do so only at higher voltages continuously because it uses a linear regulator that overheats at high voltage drops and modest current.

The electrolyte temperature stabilised at about 60-70 C, at such a high temperature the anode wore down fairly quickly. Within two days the liquid was black with extremely fine graphite particles in suspension.

The evaporation of the electrolyte was slower than I expected. The vertical placement of the vent pipe acted like a reflux condenser limiting the loss rate to less than 10 ml per day. The volume was made up as required with additional saturated KCl solution.

After about five days the solution began to wick up through the threads of the electrode connections and evaporate, forming a crust of salts that grew larger and larger. There was also visible crystallisation in thin plates settling on the bottom. This crust forming process eventually destroyed the brass anode connection and a large part of the alligator clip lead, the electrode dropped to the bottom and the cell failed.

The cell failed after approximately 1005 Ah. At the expected efficiency that would have converted most of the Potassium Chloride in the electrolyte. The cell was cold when I discovered it, most of the graphite had settled out, mixed with an 40 mm thick crust of crystals in the bottom of the jar.

Processing The Electrolyte

The greenish and brown contaminated crusting around the anode was disposed of, but the clean crystals formed on the electrodes themselves were scraped off and added to the raw electrolyte. The electrolyte was diluted to 1 litre and boiled to destroy the hypochlorite and reduce the volume to about 800 ml, then half was filtered off and further boiled down to 300 ml then allowed to cool. The remaining unfiltered liquid and sludge from the filter was also allowed to cool in another container for later processing.

Approximately 70 grams of flaky crystals fell out of solution on cooling and were filtered off. Once dry I puzzled over how to purify these crystals. Looking at the solubility curve for Potassium Chloride I figured that if I assume they were 100% Potassium Chloride and dissolved them in 100 ml per 30 g then cooled the solution to room temperature nothing would precipitate. I tested this experimentally dissolving 30 g of pure Potassium Chloride in 100 ml of water by heating, nothing precipitated on cooling.

So in went the 70 g of raw crystals into 200 ml or so of water. A quick boil and into the fridge to cool. 15 minutes later I had what I would later measure as 55 g of clearly monoclinic crystalline product. The

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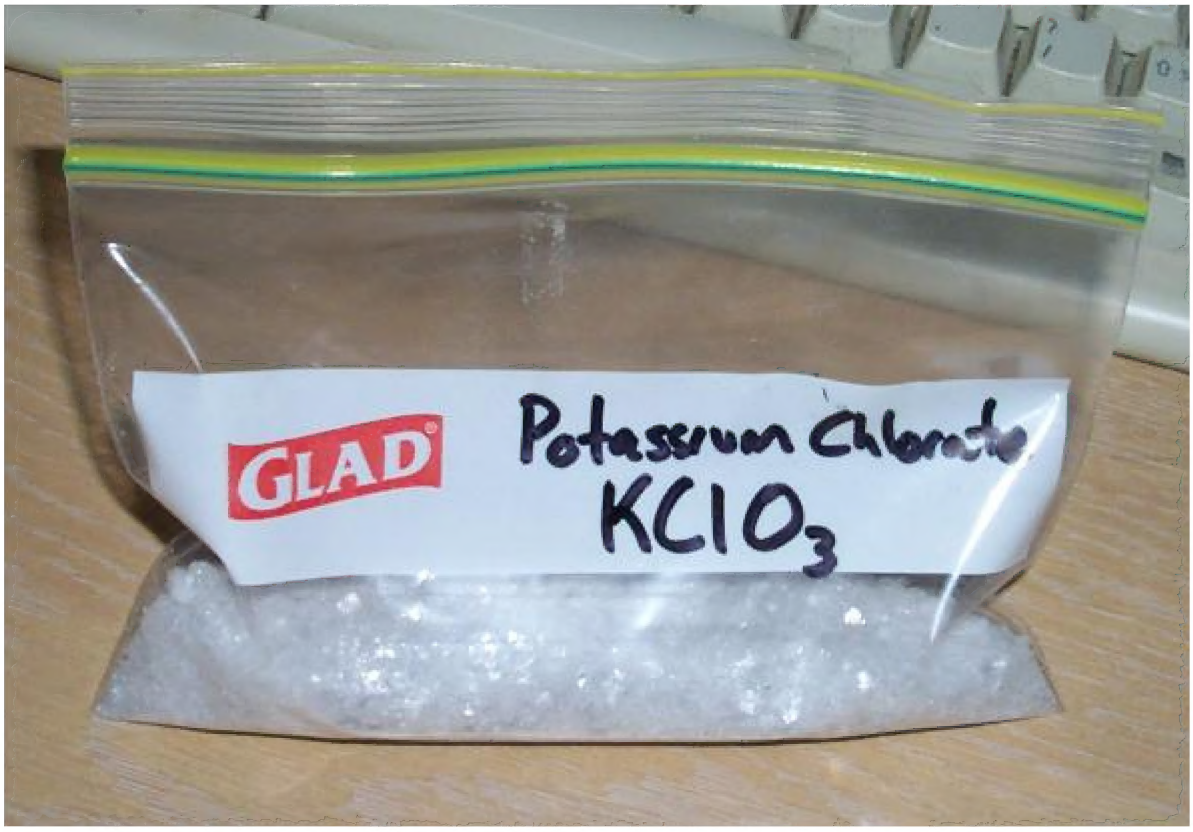
remaining liquid was boiled down a little and added to the unprocessed sludge container so as not to loose any material.



But was it really Potassium Chlorate, and was it contaminated with too much Sodium to be useful?

Tests

Your most basic of tests to start with; will it burn something? A few grams of Lancaster Chlorate Red #3 was prepared. It worked perfectly.

A truly beautiful red. Very pure, no significant Sodium contamination, but a blue would be a better test. The yellow/white in the picture is mainly due to overload of the camera, the illuminated smoke shows the true flame colour. Of course there is some incandescent carbon in the flame that makes it more orange to the eye than the actual majority of the radiated light.

A small amount of H3 was prepared. Even just screened together it burnt very rapidly with a violet/white light. It sure appears to be Potassium Chlorate.

Lessons and Comments

Make the electrical connections to your electrodes outside the cell, protected from creeping crystals with

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amount of Copper ions from the dissolved Brass anode connection. Copper is a powerful sensitiser for Chlorate, there are *many* recorded accidents with Copper and Chlorate, quite a few involving Copper heat exchangers in Chlorate factory evaporators. I believe I was able to minimise and remove the Copper contamination, but it is something to consider if you try this yourself.

There is much Chlorate left in the mother liquor. I hope to extract, or at least recycle it back into the next run. On cooling much of it crystallised out on top of the settled anode mud. The fine graphite particles probably acting as nucleation sites for crystallisation. Some larger crystals were removed and studied, they were somewhat imperfect flat rhombic prisms often including graphite particles in their defects. Some looked more like hexagon prisms, like the one in the photo. No doubt the influence of the high Chloride concentration on the growing process also contributed to the non text-book monoclinic crystal shape.

The erosion of the anode was fairly severe, about half its volume was lost. If it had run the full month for complete conversion I doubt there would have been much left of the anode. The rate of erosion would only have increased once the Chloride level dropped to virtually nothing and Perchlorate production started. It might be reusable as a cathode, or perhaps an anode at low temperatures in the chlorate cell. The remaining brass material would need to be removed and the electrode cleaned carefully though.

Better anode material is definitely required for the cell. I've investigated MMO/Ti and Pt/Nb substrate electrodes from a supplier in India, I expect to get a quote soon. I'll probably faint when I read it though...

The graphite cathode and its connections remained pristine, protected by its polarity in the cell, a quick wash and it was ready for reuse. However other tests have shown there is a slight graphite erosion even from the cathode, so I think I will pursue using Titanium as the cathode material in my future cells.

I've purchased some Titanium rods on eBay to use as cathodes and anode connection and support structures. A friend in the US contributed a length of Pt/Ir wire which I've yet to test.

Another observation for future reference is surface erosion of the cell container. It is only PE and was probably etched by the hot moist chlorine. The anode side of the container was the worst effected, appearing like HF etched glass used in privacy screens. PP or a fluoro-polymer would probably be a better material for a long-life cell. The solution when first filtered appears yellow/green from elemental Chlorine in solution, boiling helps drive its reaction with the cathodic Hydroxide to form additional Chlorate and its evaporation out of the water.

8 comments.

Parent article: Making Chlorates and Perchlorates.

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